Case file notes for Pavillion, WO#1104012
Submitted by Jennifer L. Gundersen, OASQA Chemist

Samples were analyzed for diethylene glycol (DiG) (CAS# 111-46-6), triethylene glycol (TriG) (112-27-6), tetraethylene glycol (TeG) (112-60-7) and 2-butoxyethanol (2-Bu) (111-76-2) by LC/MS/MS (Waters TQD-LCMSMS) on a Waters Atlantis dC18 3um 2.1 x 150mm column (s/n- 0141301481).

Samples 1104012-09 and 1104012-10 are not included in this Work Order. Refer to Results discussion below.

An HPLC/MS/MS method does not currently exist for these analytes. EPA SW-846 Methods 8000C and 8321 were followed for method development and QA/QC limits, where applicable. All applicable OASQA On Demand QA/QC procedures were followed, where appropriate.

Samples were injected without extraction onto the LC/MS/MS system. An appropriate surrogate has not yet been identified.

MS tuning and calibration:
Exact mass calibration is done annually with the preventive maintenance procedure. Mass calibration was successfully performed according to manufacturer's direction with NaCsI on 6/17/2010.

The system was tuned with authentic individual standards of each compound according to manufacturer's directions using the Waters Empower "Intellistart" tune/method development program in the MRM (multiple reaction monitoring) ESI+ (electrospray positive) mode. Tune data, with standard information, is included in the case file. Target masses, transition data and voltages determined in each tune for each compound were compiled into one instrument method set. Only one MS tune file (which determines gas flow rates and source temperatures) may be used during a sample set. For these samples, the tetraethylene glycol tune was used as it provided the best response for all targets. For future analyses, a separate tune for 2-butoxyethanol will be investigated.

A second MRM mass transition was monitored for confirmation of each target. The response of the confirmation MRM was generally much lower that that of the primary MRM. While calibration curves were generated as part of the method development and concentrations were calculated, they had much higher quantitation limits than the primary MRM and were not used for reporting, only for verification. If the concentration calculated for the confirmation MRM exhibited a +/- 40% difference, the concentration should be considered estimated and the presence of the target suspect (As per Method 8000C 11.10.4).

Chromatographic method:
Due to differences in optimal chromatographic separation, the three glycols were analyzed in one sample set and 2-Bu was analyzed separately.

Initial and continuing calibration:

DIM0183377

Because the method was under development when samples arrived, a wide range of initial calibration standard concentrations were prepared. Initial calibration standards from an UltraScientific custom standard mix were prepared at 1000, 100, 50, 25, 10 and 5ug/L (ppb) for testing linear ranges. The second source calibration verification (SCV) standard was a custom mix from AccuStandard. Over the course of several days of preliminary analyses, the recovery of triethylene glycol in the SCV was approximately half of the value expected by initial calibration. Both the initial calibration standard and SCV standard were prepared from custom stock standards containing all target analytes. Both manufacturers were contacted to determine whether standard preparation or analyte purity could be the problem. An email from Accustandard (included in the case file) confirmed that the concentration of TriG in their standard was incorrect. Because of these problems, there is no SCV for TriG. New standards have been received and will be used in future analyses.

Because several quality control criteria (matrix spike/duplicate, CCV and SCV percent recoveries) were outside of QC limits, all positive results should be considered estimated and have been qualified "J". Recoveries will be tracked to determine if default criteria in Method 8000C are appropriate.

Because there was no extraction associated with this sample set, CCV samples were also used as blank spike (BS) samples. According to OASQA On Demand procedures, a blank spike should be prepared at the NQL. Because the method was still under development and the NQL had not been determined, the CCV/BS samples were analyzed at a concentrations of 50ppb, which is above the NQL for 2-Bu, TriG and TeG.

A sample set run on 4/22/11 for the glycols indicated numerous problems with calibration and results are not included in this report. Raw data is included in the case file.

Matrix Spikes:
Samples 1104012-05 and 1104012-15 were prepared as a matrix spikes and duplicates. In a 10ml volumetric flask, 0.5 ml of 1ppm standard # 1100267 was spiked into 9.5ml of sample for a spike concentration of 50ppb of each target. For future work, a higher concentration spiking solution will be prepared so that the spike volume is less that 5% of the total sample volume.

Due to the high concentration of diethylene and triethylene glycol in 1104012-15, some recoveries and RPD (Relative Percent Difference) are outside of QC limits.

For sample 1104012-05, several recoveries are below criteria; this could be the result of matrix effects.

QC note:
Because the method was being developed as samples were being analyzed, it is not known if the QC data for percent recoveries and RPDs are appropriate. Most values were within or close to the default limits set forth in SW-846 Method 8000C of 80-120% for BS, CCV and SCV and 70-130% for matrix spikes and RSD of 25% but several outliers were noted. Values will be evaluated with future results to develop appropriate QC criteria.

Not knowing appropriate holding times, a holding time of 14 days was suggested. Samples 1104012-01, -02, -03, -04 and -05 were analyzed for DiG, TriG and TeG on 5/3/2011, one day after the suggested holding time. This is not expected to affect results but non-detects have been flagged "UL". Please see the report for the definition of the qualifier.

Method and instrument blanks:
Instrument blank (LCB, also referred to as IBL in the Quality Manual) and Method blank (BLK) samples (DI H2O) were analyzed concurrently since there was no extraction.

Some blanks and samples (including the trip blank and field blanks, 1104012-11, 1104012-12 and 1104012-21, as well as 2 LCBs) indicated very low levels of TeG in both the main and confirmation channel, but this may be the result of background noise or a co-eluting interference. Note that the concentration of TeG in the confirmation MRM is often almost 10x higher than the primary MRM, and thus outside of the +/- 40% difference criteria. This suggests the result is not representative of the target analyte. Affected sample results have been flagged "B"

Results:
Because several QC criteria were outside default criteria, all positive results should be considered estimated and are flagged "J".

Samples 1104012-08, -09 and -10 were supplied to evaluate holding time effects on samples stored in amber glass 40mL VOA vials with Teflon® lined caps. Because the sample set run on 4/22 could not be used, short term storage effects could not be evaluated but results for sample 1104012-07, prepared on 4/22/11 and -08, prepared on 5/3, appear to have very similar results. Samples 1104012-09 and 1104012-10 will be analyzed at a later date. Samples 1104012-09 and 1104012-10 are not rincluded in this Work Order.

Because the results in 1104012-07 for 2-Bu were below quantitation limits, the holding time test samples, 1104012-08, 1104012-09 and 1104012-10 were not run for 2-Bu.

Results for DiG in 1104012-06, -07 and -08 were above the highest calibration level and are flagged "J". For additional holding time studies, a 2x dilution will be made.

Results for TeG in 1104012-06, -07, -08 and -15 are flagged "BJ" due to blank contamination. The concentrations in these samples are less than 10 times the concentration in several blanks, resulting in the B qualifier. The confirmation MRM is within +/- 40% of the primary MRM, suggesting the concentration is likely a valid result.

Trace levels of 2-Bu were detected in samples 1104012-01, -05, -06, -07 and -15. (sample -08 was not analyzed for 2-butoxyethanol as noted above). The levels were below the quantitation limit (BQL) but it should be noted that both the primary and confirmation MRMs indicated the presence of 2-Bu in all samples listed above except for 1104012-01 where only the primary MRM was present. For future sample events, attempts will be made to lower the NQL for 2-Bu.